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MAGNETIC ORDERING IN OXIDE SOLID SOLUTIONS. (U)
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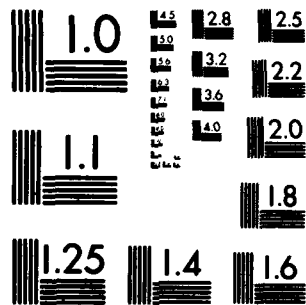
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20. ABSTRACT (Continue on reverse side if necessary and identify by block number) Powder neutron diffraction, magnetic susceptibility and Mossbauer spectroscopy have been used to investigate solid solutions based upon MnO, FeO, CoO and NiO, and we have completed measurements on NiO-CoO, MnO-CoO, NiO-MnO, FeO-MnO and FeO-CoO. In each system we have examined the changes of spin direction and crystal symmetry as a function of temperature and composition in the anti-ferromagnetic phases. The results show that the strength of the magnetic anisotropy associated with the metal ions falls in the sequence $Co^{2+} > Mn^{2+} > Fe^{2+} > Ni^{2+}$. This order is different from that found in mixed fluorides of		

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the type $K_2F_4(Co^{2+} > Fe^{2+} > Mn^{2+} > Ni^{2+})$, and we have considered, in some detail, the unexpected weakness shown by Fe^{2+} in our materials.

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Magnetic Ordering in Oxide Solid Solutions

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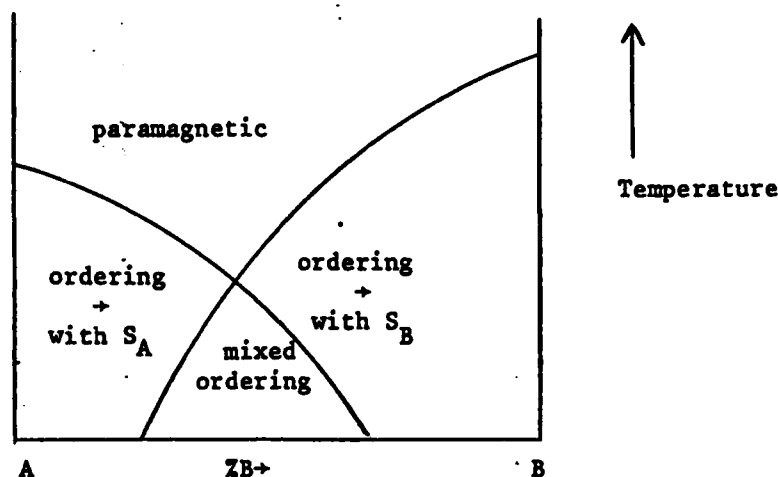
Sections 1, 2 and 3 describe the background to this work and sections 4 - 9 summarise the results we have obtained with AFOSR support during the period of our grant (1979/81).

1. Magnetic ordering in transition metal oxides has been extensively studied by susceptibility and neutron diffraction techniques, and the nature of the magnetic interactions in systems containing one type of paramagnetic ion is well understood. Ternary oxides containing more than one type of cation site (e.g. spinels) have also received much attention and the origins of their magnetic properties are again well known. We are presently focusing our attention on the magnetic ordering characteristics of some simple oxide solid solutions in which the two paramagnetic ions occupy the same type of site, but have competing anisotropies. These are solid solutions of the first transition series monoxides MnO, FeO, CoO and NiO; they adopt the sodium chloride structure. Our results will have implications for the magnetic behaviour of a wide range of materials.

2. Neutron diffraction studies on MnO and NiO have shown that they undergo rhombohedral distortions ($\alpha > 60^\circ$) below their Néel temperatures and in each compound the spin direction is within the (111) plane.¹ On the other hand, CoO exhibits a tetragonal distortion with the spin tilted 27.4° away from the unique axis.² Ferrous oxide is non-stoichiometric and we have recently examined the influence of defect clustering upon its magnetic properties;³ its symmetry is rhombohedral and the spins point along the [111] axis.

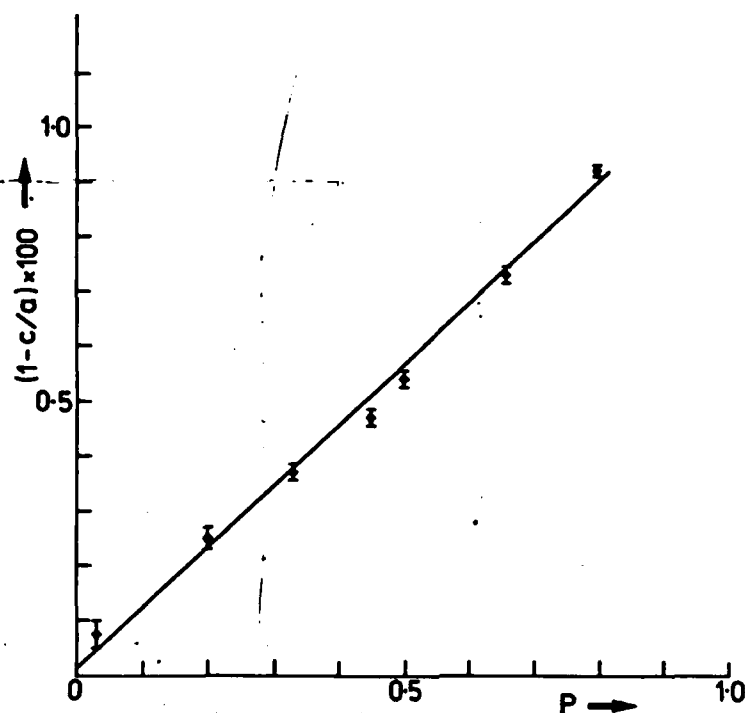
3. The first row monoxides are known to form solid solutions, but the effect of the ensuing disorder upon the magnetic structure has not been investigated

experimentally. This problem is of current theoretical interest, and renormalisation group calculations have recently been reported for several types of disordered systems.⁴ The result of a treatment for systems containing spins with competing anisotropies is shown below:



4. The systems NiO-CoO, MoO-NiO, MnO-CoO, MnO-FeO and CoO-FeO have been examined as a function of composition by neutron diffraction on the high resolution powder diffractometer, D1A, at the high flux beam reactor in Grenoble. Magnetic susceptibility and Mössbauer spectroscopy measurements have also been carried out on the solid solution MnO-FeO. Our experiments have shed new light on the magnetic anisotropies of transition metal ions in mixed metal oxides, and have also yielded new information about the defect structure of solid solutions based upon non-stoichiometric ferrous oxide.

5. In the system NiO-CoO, we have analysed data at several compositions by profile analysis techniques.⁶ The magnitude of the observed magnetic moments indicates that the spins are collinear at all compositions, and in the range CoO-Co_{0.10}Ni_{0.90}O the spin direction remains the same as that in CoO itself. This remarkable observation reflects the very strong single ion anisotropy of Co²⁺, an effect which is also apparent in the linear dependence of the tetragonal c/a ratio upon the mole fraction, P, of CoO:



Refinements on a sample of composition $\text{Co}_{0.05}\text{Ni}_{0.95}\text{O}$ show that the spin makes an angle of 33° with $[001]$, intermediate between CoO and NiO , and a small monoclinic distortion of the unit cell arises from the superposition of both rhombohedral and tetragonal symmetry. Molecular field methods have also been used to calculate the temperature dependence of the strain and magnetisation.

The results of this study were presented at the International Conference on Magnetism and Magnetic Materials (New York, 1979) and published in the Journal of Applied Physics.⁷

6. In contrast to NiO-CoO , the addition of MnO to CoO reveals a more evenly balanced contest between anisotropies of Mn^{2+} and Co^{2+} . Unlike the single-ion behaviour of Co^{2+} , the anisotropy of Mn^{2+} depends upon multiple-ion effects, in particular the dipole-dipole interactions between the high-spin $d^5 \text{Mn}^{2+}$ ions. There is also a strong ligand field anisotropy arising from $\text{Mn}^{2+}\text{-Mn}^{2+}$ exchange; this is responsible for the large rhombohedral distortion in MnO , itself. Our results for MnO-CoO show that the superposition of the tetragonality of CoO and the rhombohedral distortion of MnO leads to a pronounced monoclinic distortion at intermediate compositions (25 - 75% MnO). In this range, the spin direction is intermediate between that of CoO and MnO , but it is clear that the spins are

collinear at all compositions. The lattice parameters, and the magnitudes and directions of the magnetic moments, reveal three distinct regions of behaviour in $\text{Mn}_x\text{Co}_{1-x}\text{O}$. In the Co-rich regime ($x < 0.36$), the orbital moment of Co^{2+} is partially quenched and distortions characteristic of both Jahn-Teller and magnetostrictive stabilisations are observed; the spin directions are close to that of CoO. For $0.51 < x < 0.66$, spin only Co^{2+} moments and Jahn-Teller distortions only are evident. However, when Mn^{2+} is in large excess, indications of a magnetostrictive Co^{2+} distortion reappear, presumably because the Co^{2+} concentration is insufficient to support a cooperative Jahn-Teller distortion, and the moment is confined to the (111) plane.

7. Because of the similarity between the magnetic structures of MnO and NiO, we initially anticipated that solid solutions between them would be uneventful with collinear spins and a linear change in rhombohedral angle, α , with composition. Surprisingly, the latter expectation has not been fulfilled and samples with compositions 22, 53 and 81% MnO all appear to be essentially cubic, even at 4.2K, with collinear spins in the (111) easy plane. The results are summarised below:

Cell parameters of MnO, NiO and their Solid Solutions.

NiO	$a=b=c = 2.946\text{\AA}$, $\alpha=\beta=\gamma = 60.20^\circ$.
$\text{Ni}_{0.78}\text{Mn}_{0.22}\text{O}$	$a=b=c = 2.995\text{\AA}$, $\alpha=\beta=\gamma = 60.05^\circ$.
$\text{Ni}_{0.47}\text{Mn}_{0.53}\text{O}$	$a=b=c = 3.042\text{\AA}$, $\alpha=\beta=\gamma = 60.04^\circ$.
$\text{Ni}_{0.19}\text{Mn}_{0.81}\text{O}$	$a=b = 3.098\text{\AA}$, $c = 3.106\text{\AA}$, $\alpha=\beta = 60.03^\circ$, $\gamma = 59.94^\circ$.
MnO	$a=b=c = 3.120\text{\AA}$, $\alpha=\beta=\gamma = 60.704^\circ$.

The absence of a significant rhombohedral distortion at all compositions is unexpected, but we now believe that it can be understood in terms of the nature of $\text{Mn}^{2+}-\text{Mn}^{2+}$, $\text{Ni}^{2+}-\text{Ni}^{2+}$ and $\text{Mn}^{2+}-\text{Ni}^{2+}$ exchange interactions. Whilst the homopolar interactions are certainly antiferromagnetic, it is known that the $\text{Mn}^{2+}-\text{Ni}^{2+}$ coupling is intrinsically ferromagnetic.⁸ The three exchange strictions are therefore in competition and tend to cancel giving an approximately cubic cell.

8. For both MnO-FeO and CoO-FeO, neutron measurements at room temperature (ie. in the paramagnetic region) confirm that non-stoichiometry is accommodated by the

formation of defect clusters similar to those observed in ferrous oxide. Our Mössbauer results are also consistent with this model. A paper describing these results has been accepted for publication in Inorganic Chemistry.⁹

Low temperature measurements reveal that small concentrations (< 5 mole %) of Co^{2+} or Mn^{2+} will divert the Fe^{2+} moment from the [111] axis and remove the corresponding trigonal ($\alpha < 90\%$) magnetostriction. The cobaltous ion has a slightly larger effect than Mn^{2+} , and these results, together with those for MnO-CoO and NiO-CoO , suggest that the anisotropy order for the iron group monoxides is $\text{CoO} > \text{MnO} > \text{FeO} \sim \text{NiO}$. This sequence differs from that found in the mixed metal fluorides, K_2MF_4 , where $\text{Co}^{2+} > \text{Fe}^{2+} > \text{Mn}^{2+} > \text{Ni}^{2+}$.

The unexpected weakness of the Fe^{2+} anisotropy can be related to a number of factors:

i) quenching of the orbital angular momentum close to the defect clusters, ii) the unfavourable orientation of the bulk moments with respect to the magnetic dipole-dipole forces, iii) the opposition of the $\text{Fe}^{2+}-\text{Fe}^{2+}$ exchange striction when small trigonal magnetostrictions occur, and iv) the presence of alternative modes by which the orbital degeneracy can be sustained (eg. a tetragonal distortion, $c/a > 1$).

The influence of defect clustering upon the cooperative magnetic interactions has been examined in detail and the results suggest that the current model for this type of behaviour³ requires modification.

9. Publications describing our results on MnO-NiO , MnO-CoO , and MnO-FeO (at low temperatures) are being prepared. Further details of the work described above can be found in reference 10.

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